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Abstract

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STUDY OF THE COPOLYMERIZATION OF ISOPRENE AND DIVINYL WITH BUTYLLITHIUM

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At the present time, catalytic copolymerization by catalysts of a basic character has as yet been studied very little. Only a few papers have been published in which quantitative data are given ([1–5]). Judging from the values of the copolymerization constants, the monomers differ very greatly in their reactivity. The greatest activity is possessed by monomers in which the double bond of the vinyl group is conjugated with a multiple bond of a nitrile or carboxyl group. The copolymerization of diene hydrocarbons under the action of catalysts of a basic character has not been investigated up to now. It is known that in free-radical (emulsion) polymerization these hydrocarbons have relatively close relative activities ([6]).

It was of interest to establish what relative reactivity is possessed in catalytic alkaline copolymerization by the diolefin hydrocarbons isoprene and divinyl, which differ from one another only by the presence of a methyl group. To determine the composition of the copolymers, the tracer-atom method was applied. For this purpose, isoprene with radioactive carbon C^{14} was synthesized (from acetylene-C^{14}, obtained from $BaC^{14}O_3$) by the slightly modified method of A. E. Favorskii ([7]). The joint and separate polymerization of isoprene and divinyl was carried out in hexane solution with butyllithium at 50°, at a total monomer concentration of 2 mol/l and a catalyst concentration of 0.0025 mol/l. Butyllithium was synthesized by the known procedure ([8]). Analysis of the butyllithium solution was carried out by the usual method with double titration ([8]).

For the polymerization, well-purified and dried monomers and solvent were used. All operations for charging the products into the reaction ampoules were carried out in a stream of dry nitrogen and under vacuum on a distribution manifold. The reaction ampoule consisted of two vessels separated by a partition and connected by a graduated tube. One part of the ampoule was filled with solvent and monomers; into the other was introduced the catalyst—a solution of butyllithium in hexane.

The partition of the ampoule was broken with a glass striker, and the contents of

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Fig. 2. Copolymerization curve for the isoprene–divinyl system

Figure 2: Fig. 2. Copolymerization curve for the isoprene–divinyl system

the ampoule were rapidly mixed. The polymerization was carried out in a water thermostat at 50°. The rate of polymerization was judged from the decrease in the volume of the reaction solution.

The polymerization reaction was stopped at different degrees of conversion by rapid cooling of the reaction ampoule, after which the ampoule was opened and a small amount (2 ml) of ethyl alcohol was added to decompose the catalyst. Then the unreacted monomers and solvent were distilled off from the ampoule under vacuum, and the degree of conversion was determined from the weight of the polymer dried at 60–80° ($p = 2$ mm Hg).

The compositions of the copolymers were determined from the radioactivity of the samples: polyisoprene-C^{14} was taken as the standard, its relative activity being expressed by the number of standard units in a $BaC^{14}O_3$ sample. Samples of poly-

mers were collected in small brass cuvettes (diameter 2 cm, height 0.5 cm), whose geometric position under the end-window counter was fixed. The results of the experiments are given in Table 1.

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The data obtained made it possible to calculate the copolymerization constants from the exact integral Mayo–Lewis equation [9]: $\alpha = 0.47 \pm 0.03$ (for isoprene) and $\beta = 3.38 \pm 0.14$ (for divinyl). Figures 1 and 2 show the calculated curves for the compositions of the copolymers and the experimental points plotted on them.

Table 1

Dependence of copolymer compositions on the composition of the initial mixture and the depth of conversion

Composition of initial mixture, mol. %		Copolymer composition by radioactivity, mol. %		Depth of conversion, %	Composition of initial mixture, mol. %		Copolymer composition by radioactivity, mol. %		Depth of conversion, %
isoprene	divinyl	isoprene	divinyl		isoprene	divinyl	isoprene	divinyl	
51.1	48.9	43.7	56.3	84.6	20.7	79.3	6.6	93.4	40.2
49.0	51.0	27.0	73.0	14.5	19.8	80.2	9.5	90.5	64.5
48.7	51.3	28.3	71.7	25.2	20.9	79.1	8.0	92.0	11.9
52.2	47.8	28.7	71.3	12.4	78.9	21.1	57.5	42.5	42.3
51.1	48.8	31.9	68.1	35.4	69.7	30.3	54.4	45.6	16.8
49.0	51.0	34.5	65.5	69.5	78.0	22.0	63.0	37.0	50.8

The calculation of copolymer compositions for specified initial monomer ratios was carried out graphically in the following way: the generally known integral equation for copolymerization

$$\beta = \frac{\lg \frac{B_0}{B} - \frac{1}{p} \lg \frac{1 - p\frac{A}{B}}{1 - p\frac{A_0}{B_0}}}{\lg \frac{A_0}{A} + \lg \frac{1 - p\frac{A}{B}}{1 - p\frac{A_0}{B_0}}}, \tag{1}$$

where $p = \frac{1-\alpha}{1-\beta}$, can be represented in the following form:

$$\lg \frac{B}{B_0} = \frac{\alpha\beta - 1}{(\beta - 1)(\alpha - 1)} \lg \frac{\frac{A}{B} - \frac{1}{p}}{\frac{A_0}{B_0} - \frac{1}{p}} - \frac{\beta}{\beta - 1} \lg \frac{\frac{A}{B}}{\frac{A_0}{B_0}}. \tag{2}$$

If we introduce the notation

$$\frac{A}{A_0} = x; \quad \frac{B}{B_0} = y; \quad \frac{\alpha\beta - 1}{(\beta - 1)(\alpha - 1)} = k_1; \quad \frac{\beta}{\beta - 1} = k_2; \quad \frac{B_0}{A_0} \cdot \frac{1}{p} = k_3; \quad k_4 = k_1 \lg(1 - k_3),$$

Fig. 3. Kinetic curves of polymerization

Figure 3: Fig. 3. Kinetic curves of polymerization

where A_0 and B_0 are the concentrations of the monomers at the initial moment, and A and B are the concentrations of the monomers at the moment polymerization ceases, then equation (2) takes the form:

$$\lg y + k_1 = k_1 \lg \left(\frac{x}{y} - k_3 \right) - k_2 \lg \frac{x}{y}. \tag{3}$$

A graphical solution of equation (3) makes it possible to determine the value $z = \frac{x}{y}$ for various values of y, i.e., to determine the values of A and B of interest to us.

The experimental points lie satisfactorily on the calculated curves, taking into account the errors allowed in dosing the monomers in volumetric measurement.

Fig. 3. Kinetic curves of polymerization. $C_{\text{mon}} = 2$ mol/l; $C_{\text{cat}} = 0.0025$ mol/l. a—isoprene, b—divinyl, v—isoprene-divinyl (1:1).

Figure 3 presents the kinetic curves of separate polymerization of isoprene and divinyl and of joint polymerization at a monomer ratio of $1 : 1$.

From the experimental data presented it follows:

1. In joint polymerization, the more active monomer is divinyl ($\beta > 1$; $\alpha < 1$).
2. In separate polymerization, the more active monomer is isoprene, which polymerizes at a rate approximately 3 times greater than divinyl.
3. In joint polymerization, the reaction rate in the initial stage corresponds to the rate in separate polymerization of divinyl.

An analogous phenomenon is observed in the copolymerization of styrene with divinyl under the action of butyllithium ([5]). In separate polymerization, styrene polymerizes many times faster than divinyl. In copolymerization, divinyl initially polymerizes at a rate corresponding to separate polymerization, and only after its practically complete consumption does styrene begin to polymerize—also at a rate corresponding to its separate polymerization.

The higher reactivity of isoprene as compared with divinyl in separate polymerization is evidently due to the presence of a permanent dipole moment in the isoprene molecules owing to the positive inductive influence of the methyl group.

The phenomenon of "reversal" of monomer activity in copolymerization cannot be explained if one proceeds from the concepts of a stepwise mechanism of the polymerization reaction ([10]). Regardless of the terminal unit of the growing polymer chain:

$$\sim CH_2 - CH = CH - CH_2Li \quad \text{or} \quad \sim CH_2 - CH = \underset{CH_3}{C} - CH_2Li$$

the probability of addition of a molecule of each monomer must be determined by the activity of the monomer and by its concentration in the solution. Thus, in our case the copolymer should be enriched in isoprene.

To explain the phenomenon of the "reversal" of monomer activities, the course of the reaction may be represented as follows. In catalytic polymerization the active center is a dipole interacting with the surrounding medium; if the rate of reaction of the monomer with the dipole, which may also be an organometallic compound, is relatively low, then the dipole will be surrounded by a shell of polarized monomer molecules. The composition of the copolymer, as well as the rate of the polymerization reaction, will be determined by the concentration of monomers in such a shell. In the copolymerization of isoprene with divinyl, owing to the relatively greater mobility of the electron cloud and the smaller steric hindrance for divinyl molecules, the monomer shell evidently consists mainly of divinyl molecules. Therefore the overall rate corresponds to the rate of separate polymerization of divinyl, while the composition of the copolymer is enriched in the latter. Since in radical polymerization the active center carries no charge and is not a dipole, the formation of such a shell is excluded, and the order of addition of monomer molecules depends only on the concentration and relative activity of the monomers and of the free radicals at the ends of the growing chains; therefore the reversal phenomenon does not occur.

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Note: Figure translations are in progress. See original paper for figures.